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## CERAMIC PIGMENTS BASED ON NATURAL MINERALS

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The results of studying the use of nontraditional materials in the production of ceramic pigments are summarized. It is noted that the use of natural materials, namely, calcium-magnesium silicates, opens vast opportunities, since they can act as main or transitional crystalline structures. New methods of synthesis of pigments are discussed.

Russian scientists have developed a rich palette of ceramic pigments with diverse color shades. The production of such pigments requires substantial expense, since it involves high-temperature synthesis and use of pure chemical reagents. The use of nontraditional material in the composition of pigments would make it possible to substantially reduce their production cost.

The classification of ceramic pigments proposed by Tumanov is based on the type of crystalline structure. The crystal lattices of spinel, corundum, zircon, and garnet types are thoroughly investigated. They are synthesized from oxides and salts of various elements [1, 2]. There are numerous publications on production of ceramic pigments based on natural minerals: diopside, wollastonite, kaolin, etc. [3–7].

The Silicate Technology Department of Tomsk Polytechnic University has, for more than a decade, been researching the development of ceramic pigments based on natural minerals and industrial waste.

Rigid requirements are imposed on raw materials used for ceramic pigments regarding their purity (absence of colorant impurities) and stability of their chemical compositions. Accordingly, natural minerals satisfying these requirements have been investigated, such as Slyudyanskoe diopside and wollastonite, Alguiskoe tremolite and talc, Kholinskoe zeolite, and topazite from the Kopna deposit (Kemerovo Region). The mentioned minerals are found in Siberia and form sufficiently large deposits, or are impurity rocks in the extraction of other minerals.

The possibility of colorant ions incorporating into the crystal lattice of natural minerals without additional introduction of batch components was investigated. The most accessible and available materials were used as chromophores: salts of iron (III), cobalt (II), chromium (III), nickel (II), copper (II), and manganese (II).

It is established that minerals have different capacities for assimilating colorant ions, depending on their specific

crystal structure. Diopside pigments based on tremolite and diopside have a common pyroxene structure. In the course of transformation of amphibole into pyroxene under heat treatment of tremolite, a great quantity of chromophore ions are captured, which affects the color of pigments [5]. The process of isomorphic substitution occurs due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Ceramic pigments based on diopside and tremolite are resistant as underglaze and overglaze paints and can find wide application as ceramic colorants.

Pigments based on wollastonite  $\text{CaSiO}_2$ , in which  $\text{Ca}^{2+}$  is the exchange cation, have been found effective. These pigments are low-melting but sufficiently resistant to the dissolving effect of glazes and can be used to obtain overglaze paints and colored glazes [5].

Some pigments with interesting properties have been synthesized on the basis of zeolites that are skeleton aluminosilicates with the skeleton structure. The replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in the tetrahedra determine the negative charge of the skeleton, which is compensated by charges of mono- or bivalent cations positioned together with water molecules in the channels of the structure. These cations can be easily replaced, which creates favorable conditions for synthesis of ceramic pigments. Pigments of bright red-brown tints have been obtained on the basis of Kholinskoe zeolite (clinoptilolite  $(\text{Na}, \text{K})_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ ). They were synthesized at a temperature of 1000–1050°C, as the clinoptilolite structure disintegrates at a higher temperature. Accordingly, the use of these pigments is restricted by temperatures (low-temperature ceramic mixtures, overglaze paints) [8].

The use of natural topaz  $\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$  in producing ceramic pigments was investigated. The topaz structure in firing is rearranged into the crystal lattice of mullite. At the same time, volatile components are emitted as fluorides. The resulting pigments do not have a bright color. This is presumably due to partial volatilization of the colorant ions in the form of fluorine components and to minimum restructuring involved in the transition from topaz to mullite, which im-

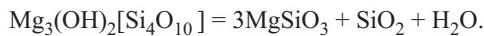
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pedes the incorporation of chromophores. However, these pigments can be recommend as shading colorants for ceramics [9].

A disadvantage of using natural minerals as the basis for pigments with preservation of their structure is the limited ionic capacity of such minerals. When a certain concentration is exceeded, the colorant ions begin to be formed as free oxides which degrade the coloring and are not always resistant to the dissolving effect of glaze at high temperatures.

Wide possibilities are opened by using the crystal lattice of natural minerals as the basis for transition to derivative crystalline structures, since a higher amount of chromophore ions can participate in their synthesis. In this way using a limited number of minerals it is possible to obtain a more diverse color palette for pigments.

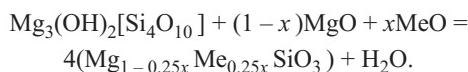
Pigments with magnesium metasilicate, forsterite, and diopside structures were synthesized on the basis of talc [10, 11]. In the decomposition of talc, magnesium metasilicate and free silica are formed:



Pigments based on talc contain excessive silicon oxide; therefore, magnesium oxide has to be added:



The synthesis of the pigments was implemented using the reaction

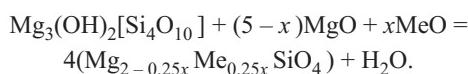


Pigments with additional magnesium oxide contain magnesium metasilicate and a small quantity of forsterite, since its formation in the reaction between  $\text{SiO}_2$  and  $\text{MgO}$  is thermodynamically preferable, and only when  $\text{MgO}$  is bound does the residual silicon oxide react with magnesium orthosilicate and form magnesium metasilicate. Pigments with the magnesium metasilicate structure contain such chromophores as  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , have a saturated color, and are resistant as underglaze paints.

Magnesium oxide in the presence of magnesium metasilicate primarily reacts with the latter and forms magnesium orthosilicate; therefore, it is easy to obtain ceramic pigments with the forsterite structure based on talc by using the respective additional components:



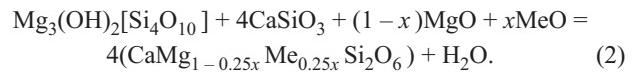
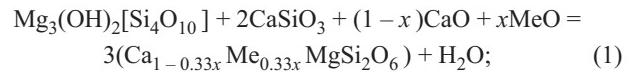
Pigments of diverse colors have been synthesized within this system:



It should be noted that different concentrations of the same chromophore yield different pigment shades. Thus, the color of iron-bearing pigments varies from beige to brown and dark brown, that of nickel-bearing pigments from light lettuce to yellow-green and dark olive, that of cobalt-bearing pigments varies from light pink to lilac and purple, etc. The pigments of the forsterite composition contain forsterite (the main phase), magnesium metasilicate, residual colorant oxides, and cristobalite. Under a longer exposure, increased firing temperature, and mineralizing additives, the content of the byproduct of the reactions decreases.

The forsterite pigment based on talc can be widely applied: from coloring ceramic mixtures and glazes to synthesizing overglaze and underglaze paints for porcelain, faience, and majolica.

The results of studying ceramic pigments with the diopside structure synthesized from oxides, as well as those based on natural minerals, are widely known. Talc is perfect for synthesis of the diopside structure, since the chain structure of magnesium metasilicate that is formed in the decomposition of talc is beneficial for the formation of the pyroxene structure of diopside. Calcium and silicon oxides can be introduced via natural wollastonite, correcting the stoichiometric composition by pure oxides. Two reactions were studied:

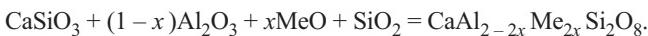
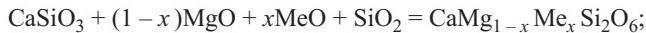


The pigments were fired at a temperature of 1200–1300°C.

The x-ray analysis indicates that reaction (1) leads to the formation of a clearly expressed diopside structure, where  $\text{MgSiO}_3$  and  $\text{SiO}_2$  are present in small quantities. The x-ray pattern of the pigment obtained according to reaction (2) in addition to diopside peaks has numerous peaks typical of  $\text{CaSiO}_3$ . The correlation of the results of synthesis carried out according to two reactions clarified their advantages and disadvantages. In the first case, the construction of a diopside structure is better implemented, but the pigments have a dull tint. The substitution takes place due to the  $\text{Ca}^{2+}$ , which is much larger than the chromophore ions. As the quantity of introduced chromophores grows due to wollastonite, the color of the pigments produced based on reaction (1) improves. In the second case [reaction (2)], a complex solid solution is formed consisting of different crystalline phases. The color characteristic of the pigments are good. The substitution process occurs due to  $\text{Mg}^{2+}$  ion, whose size is close to the ionic radius of the colorant ions.

Talc is a fairly common mineral and its use reduces the production cost of ceramic pigments. Due to the capacity of talc to form magnesium metasilicate and silica under heating, there are wide possibilities for producing ceramic pigments with different ceramic structures.

Pigments with the structures of diopside and anorthite were synthesized on the basis of wollastonite [12] according to the reactions



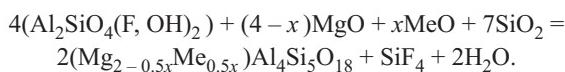
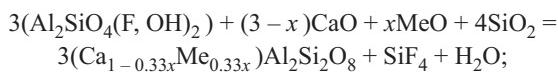
The firing was implemented at temperatures of 1100–1300°C.

The diopside chain structure differs from the wollastonite chains only in the spatial position of the  $[\text{SiO}_4]^{4-}$  tetrahedra. The incorporation of colorant ions into the diopside lattice occurs due to  $\text{Mg}^{2+}$  ions, which ensures their intense incorporation into the structure due to the proximity of the ionic radii. The reaction of synthesis proceeds in several stages, and the reaction products include solid solution of diopside, wollastonite, magnesium metasilicate, and forsterite. When part of magnesium oxide is replaced by the chromophores, cristobalite and spinels  $\text{MgFe}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  are formed. The pigments have a bright color and are promising for use as colorant for ceramic articles.

An analysis of the anorthite pigments based on wollastonite indicated that they are based on the solid solution of anorthite, wollastonite, and corundum. As the firing temperatures increases to 1300°C and a mineralizer is added, the yield of anorthite grows. Small chromophore additives also have a mineralizing effect and contribute to increasing the yield of anorthite. As the content of the colorant oxides increases, the intensity of the anorthite peaks decreases. Chromium and iron ions are mostly released in their free form with a weight content of about 16%. Cobalt pigments, along with anorthite, contain spinel  $\text{CoAl}_2\text{O}_4$ . The pigments have a bright saturated color and are resistant to the effect of glaze and to high temperatures.

One can obtain other crystalline structures based on the wollastonite structure, which makes it possible to expand the palette of ceramic pigments and to more extensively use natural mineral materials.

Based on topaz  $\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$  with additional introduction of  $\text{CaO}$  and  $\text{MgO}$ , pigments with the crystal structures of anorthite and cordierite, respectively, were synthesized [13]:



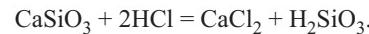
The pigment palette varied from dark blue, light blue, and green tints to red-brown, dark brown and black, depending on the type and the concentration of the chromophore. The pigments are resistant to high temperatures and to the aggressive action of glaze and have diverse pleasant tints.

An x-ray phase analysis was carried out on a DRON-3M set. It was established that, in addition to cordierite and anorthite, the products of the reactions contain mullite and cristobalite. This indicates a gradual multistage type of synthesis. The pigments with  $\text{CoO}$  contain spinel  $\text{CoAl}_2\text{O}_4$ . Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) exists in the free form in both reactions. One can infer that adding chromophores does not intensify the main reactions of mineral formation, since the crystallinity of the structure, its regularity, and symmetry deteriorate, which is indicated by a sharp decrease in the intensity and clarity of the main diffraction peaks, compared to the reference samples.

Pigments based on proper topaz (without additional batch components) with the crystal structure of mullite have significantly less bright coloring than pigments with derivative structures of anorthite and cordierite. The obtained pigments have increased resistance to fluxes, glazes, and high temperatures and are suitable for wide application in ceramic industry.

The studies carried out at the Silicate Technology Department are intended not only to expand the list of available raw materials for ceramic pigments but also to develop new methods for their production.

The stage of gel formation was used in the synthesis of pigments based on natural wollastonite [14]. With a small additive of hydrochloric acid, the crystalline lattice of wollastonite transforms into a gel-like state, as silica gel and calcium chloride are formed:



This makes it possible to achieve a high degree of homogenization and averaging of the mixture components. In firing, the crystal structure of wollastonite is restored (already at 1050°C), which is beneficial for the incorporation of colorant ions. It is established that pigments based on gel-like wollastonite have a brighter color than pigments based on natural wollastonite produced without the stage of gel formation. The gelling method can be used to synthesize ceramic pigments not only with the wollastonite structure but with the diopside structure as well (adding magnesium salts to wollastonite).

Furthermore, a method was proposed for making ceramic pigments (USSR Inventor's Certif. No. 1353787) based on natural diopside by tinting mineral previously crushed to dispersion of 60  $\mu\text{m}$  by means of boiling in salt solutions with bivalent chromophore cations, whose ionic radii are close to the radius of calcium ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ). After boiling in these solutions, calcium cations are formed, which is due to isovalent ionic exchange in the calcium positions in the subsurface layer. As a consequence of this treatment, pink, lettuce and emerald pigments are obtained. After subsequent firing, the tint of some of them disappears or changes. Green, blue, and brown pigments have been tested and implemented in production as underglaze ce-

ramic paints. The pigments after the boiling treatment not subjected to firing can be used to tint cement, concrete, etc.

Since diopside particles in boiling become tinted in the surface layer and the tint is not always permanent, experiments were carried out making ceramic pigments using autoclave treatment, i.e., hydrothermal treatment of batch under pressure. It was expected to intensify the penetration of colorant ions into the depth of material using autoclave treatment. Natural minerals (tremolite, zeolite, diopside, wollastonite) were mixed with chromophores and subjected to hydrothermal treatment at a pressure of 0.8 – 1.2 MPa. The dried mixtures were fired at temperatures of 950 – 1200°C. The resulting pigments had bright and diverse colors; moreover, some of them, for instance, pigments with the chromophore Cu<sup>2+</sup>, could not be synthesized by the traditional method. Hydrothermal treatment facilitates the incorporation of colorant ions into the mineral lattice and decreases the temperature of synthesis of pigments by 200 – 300°C.

Thus, the use of natural minerals is promising for production of ceramic pigments. This makes it possible to use local inexpensive materials and synthesize pigments of a wide color range at relatively low temperatures.

The limited ionic capacity of natural crystalline structures can be compensated by using not only traditional methods for pigments production but also derivative crystalline structures based on the natural mineral lattice. The same approach helps to solve the problem of fully using raw materials extracted in mining.

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